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Laser Coherent Control of an Ensemble of Randomly Oriented Chiral Molecules

B. Grishanin[1], H. Takahashi[2], Yu. Vladimirova[1], D. Zhdanov[1], and V. N. Zadkov[1, *]
[1] *Faculty of Physics and International Laser Center, Lomonosov Moscow State University, Moscow, 119899 Russia*
[2] *Department of Chemistry, Waseda University, Tokyo, 169-8555 Japan*
*e-mail: zadkov@comsim1.phys.msu.ru
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Abstract—We discuss applications of laser coherent control for asymmetric synthesis of enantiomers from a racemic mixture of chiral molecules. General symmetry requirements on the exciting laser field configurations are derived. Detailed calculations are made for the example of the simplest chiral hydrogen peroxide molecule, including laser distillation scenarios from a racemic solution and estimates for induced chirality.

1. INTRODUCTION

Preliminary studies show that methods of laser physics can help in resolving one of the key issues of practical importance in the field of molecular chirality: whether laser physics and nonlinear optics can be used for preferential synthesis of a required type of enantiomers from an initially racemic mixture of molecular enantiomers. An affirmative answer to this crucial question would open new horizons for a number of applications in chemistry, medicine, and pharmacy.

A key quantum-mechanical characteristic that determines an excess of L enantiomers in an ensemble of left- and right-handed enantiomers, i.e., the degree of its nonracemicity, is the chirality operator or the degree of chirality, which can be written as

$$\hat{\chi} = \sum_i (|L_i\rangle\langle L_i| - |D_i\rangle\langle D_i|). \qquad (1)$$

The eigenvectors of the chirality operator are $|L_i\rangle$ and $|D_i\rangle$ states, and the corresponding eigenvalues are ±1. The left- and right-handed energetic states of the chiral molecules we can rewrite in the form of symmetrical and antisymmetrical composition of the symmetric and antisymmetric (in relation to the inversion operator) chiral states $|S_i\rangle$ and $|A_i\rangle$: $|L_i\rangle = 1/\sqrt{2}(|S_i\rangle + |A_i\rangle)$ and $|D_i\rangle = 1/\sqrt{2}(|S_i\rangle - |A_i\rangle)$. The chiral enantiomers are stable when the potential barrier separating the left and right minima of the double-well potential is large and the tunneling time is long (for complex organic molecules, it would be years or even millions of years). In the other limiting case, when the potential barrier is small and, respectively, the tunneling time is short, we have the so-called case of dynamical chirality in which the chiral molecule rapidly transfers from one enantiomer to another. In this case, the chiral properties show an oscillating character, and, on average, we always have a racemic ensemble of chiral molecules independent of its initial state.

A specific aspect of the chiral molecule–laser field interaction can be revealed either via magnetodipole [1] or nonlocal quadrupole [2] interactions, which are essential and can, therefore, be used for laser asymmetric synthesis of enantiomers from a racemic mixture only for large polyatomic molecules.

For small molecules, another physical mechanism can be used for asymmetric synthesis. Specifically, one can entangle the internal rotational dynamics of the molecule with the dynamics of other degrees of freedom. Keeping this in mind, one can suggest two fundamentally different schemes for preferential synthesis. One of them is based on preferential selection of left- (L) or right-handed (D) enantiomers from a racemic mixture with no change in the nuclear configurations of the molecules. The other is based on photoinduced synthesis of a required type of enantiomers from the others using methods of coherent control. Such synthesis is called laser distillation [3–9] and may be quite efficient for preliminarily aligned ensembles of molecules for practical applications by contrast with the preferential selection schemes, which turned out to be inefficient.

Unfortunately, these methods have to be modified in order to work with a racemic ensemble of randomly oriented chiral molecules. One of the principles here is dictated by the symmetry rules, and one must use the laser scenarios with the noncoplanar configurations of the laser field polarizations [10–13].

In this paper, we propose a new mechanism for controlling chiral states in simple chiral molecules with internal rotation that employs the coherent quantum entanglement of the rotational–torsional states of the molecules (it requires no preliminary spatial alignment of the molecules in a solution). Also, novel scenarios for the preferential laser synthesis of enantiomers from a racemic solution of chiral molecules employing this new mechanism of inducing chirality are proposed and analyzed in detail, and an experimental scheme realizing these scenarios is discussed. All numerical esti-

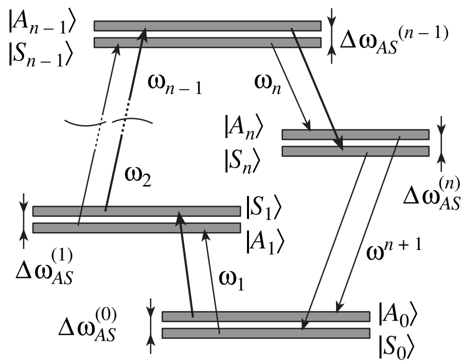

Fig. 1. Laser distillation scenario for the case when one can neglect splitting $\Delta\omega_{AS}^{(i)}$ of the chiral sublevels; i.e., $\omega_{AS}^{(i)} \ll \Delta\omega^{(i)}$ ($\Delta\omega^{(i)}$ is the spectral width of the ith laser pulse). Levels $|S_0\rangle$ and $|A_0\rangle$ are coherently linked with $n + 1$ resonance dipole transition.

mates are made for the hydrogen peroxide chiral molecules.

The paper is organized as follows. In Section 2, we analyze possibilities for inducing molecular chiral states with the help of lasers. In Section 3, we explicate the analysis in application to the hydrogen peroxide molecule and discuss various laser distillation scenarios for both inducing chirality and detecting it in a racemic ensemble of chiral molecules. Finally, conclusions are given in Section 4.

2. KEY PRINCIPLES OF CONTROLLING MOLECULAR CHIRALITY IN AN ENSEMBLE OF RANDOMLY ORIENTED CHIRAL MOLECULES

In the following, we will consider laser distillation scenarios for molecules with small—by contrast with all other characteristic splittings—frequency splitting between the chiral states $|S_i\rangle$ and $|A_i\rangle$. Here, $i = 0, 1, \ldots, n$ designates the sets of quantum numbers for those chiral doublets of the molecule that are used in the laser distillation scenario. Note that the chiral splitting is fairly small in the ground electronic state for the ground ($i = 0$) and low-lying vibrational states for most small inorganic molecules.

In order to induce chirality, one needs to create a coherent superposition of chiral states $|S_i\rangle$ and $|A_i\rangle$ or, in other words, to link them coherently via a chain of transitions through n excited states (Fig. 1).

Chirality operator (1) in the basis $\{|S_0\rangle, |A_0\rangle, \ldots, |S_n\rangle, |A_n\rangle\}$ of the eigenstates of the Hamiltonian $\hat{H}_0$ of free molecular motion with eigenenergies $E_i^{A,S}$ can be written as the tensor product $\hat{\chi} = \hat{\sigma}_1 \otimes \hat{I}$, where $\hat{\sigma}_i$ are the Pauli matrices and $\hat{I}$ is the unit operator, which is represented with an $(n + 1)$-dimensional matrix. The matrix corresponding to $\hat{\chi}$ has no nonzero diagonal elements. Therefore, by analogy with the dipole moment of the Raman transition, the sign and amplitude of the induced chirality depend on the sum of $(n + 1)$ phases of the pulses inducing transitions between the ro-vibrational levels, whereas the phases are taken with the "–" sign for the transitions in the low-lying level. Thus, changing the phase of any of the pulses used in the scenario by π will result in a change in the sign of the degree of chirality.

Let us analyze first a case of stable chiral configurations: $\omega_{AS}^{(i)} = (E_i^A - E_i^S)/\hbar = 0$. Let the ladder of transitions $|X_i\rangle \Rightarrow |Y_j\rangle$ ($X, Y = S, A$) be excited with a sequence of $(n + 1)$ nonoverlapping laser pulses $\mathbf{E} = \mathbf{e}_k A_k(t)\cos(\omega_k t + \varphi_k)$ ($k = 1, \ldots, n + 1$), while the interaction Hamiltonian $H_I^{(k)}$ is described in the rotated wave approximation (RWA) by

$$\begin{aligned} &H_I^{(k)[a]}(t) \\ &= \hbar\Omega_k(t)[\exp(-i\varphi_k)(|S_j\rangle\langle A_i| + |A_i\rangle\langle S_j|) + \text{h.c.}], \\ &\text{if} \quad X \neq Y; \\ &H_I^{(k)[s]}(t) \\ &= \hbar\Omega_k(t)[\exp(-i\varphi_k)(|S_j\rangle\langle S_i| + |A_i\rangle\langle A_j|) + \text{h.c.}], \\ &\text{if} \quad X = Y, \end{aligned} \tag{2}$$

where $\Omega_k(t) = A_k(t)d_{ij}/\hbar$ are the Rabi frequencies (d_{ij} is the matrix of the dipole moment operator). Let us rewrite the chirality operator in the form $\hat{\chi} = i\hat{\chi}_1\hat{\chi}_2$, where $\hat{\chi}_1 = \hat{\sigma}_3 \otimes \hat{I}$, $\hat{\chi}_2 = \hat{\sigma}_2 \otimes \hat{I}$. Taking into account that $[\chi_{1,2}, H_I^{(k)[s]}(t)] = 0$, $[\chi_{1,2}, H_I^{(k)[s]}(t)]_+ = 0$, $[\chi, H_0] = 0$ and designating the evolution operators that describe (2) in the interaction representation, the molecule's own free dynamics, and the density matrix of the initial (achiral) state as $U_I^{[a,s]}$, U_0, and $\hat{\rho}_0$, respectively, we have

$$\begin{aligned} \chi &= \text{Tr}\ldots(U_I^{(k)[s]})^{-1}\ldots(U_I^{(l)[a]})^{-1}\ldots(U_0)^{-1}i\hat{\chi}_1\hat{\chi}_2U_0 \\ &\quad\times\ldots U_I^{(l)[a]}\ldots U_I^{(k)[s]}\ldots\hat{\rho}_0 \\ &= i\,\text{Tr}\,\hat{\chi}_1(\ldots(U_I^{(k)[s]})^{-1}\ldots U_I^{(l)[a]}\ldots) \\ &\quad\times(\ldots(U_I^{(l)[a]})^{-1}\ldots U_I^{(k)[s]}\ldots)\hat{\chi}_2\hat{\rho}_0 \\ &= i\,\text{Tr}[\hat{\chi}_1\hat{\chi}_2\hat{\rho}_0] = 0. \end{aligned} \tag{3}$$

This result can be easily generalized in the case of overlapping pulses, as well as in the case of frequency splitting $\omega_{AS}^{(j)} \neq 0$ that does not depend on j.

In accordance with Eq. (3), the sequence of laser pulses acting on the racemic ensemble of chiral molecules does not, on average, change the ensemble's racemicity, but the chirality $\chi^{(i)}$ of the molecules in ith excited state can differ from zero. Specifically, if a molecule was initially in the ground state $\hat{\rho}_0 = 1/\sqrt{2}\,(|S_0\rangle\langle S_0| + |A_0\rangle\langle A_0|)$, then one of its enantiomers will be predominantly excited to the nth vibrational level:

$$\chi^{(0)} = -\chi^{(n)} = \frac{\tilde{\chi}}{2}, \tag{4}$$

$$\begin{aligned}\tilde{\chi} &= \cos(\varphi_1 + \ldots + \varphi_{n-1} - \varphi_n - \varphi_{n+1})\\ &\times \sin\left[2\int\limits_{t_1}^{t_1+\tau_1}\Omega_1(t)dt\right]\ldots\sin\left[\int\limits_{t_{n-1}}^{t_{n-1}+\tau_{n-1}}\Omega_{n-1}(t)dt\right]\\ &\times \sin\left[\int\limits_{t_n}^{t_n+\tau_n}\Omega_n(t)dt\right]\sin\left[2\int\limits_{t_{n+1}}^{t_{n+1}+\tau_{n+1}}\Omega_{n+1}(t)dt\right] \neq 0.\end{aligned} \tag{5}$$

Thus, for the case of $\omega_{AS}^{(i)} = 0$, implementing the chain of the transitions discussed above could be the first stage of laser distillation, and one of the stereomutation scenarios in application to the molecules in the ground or nth excited states could be the second stage.

In molecules showing dynamical chirality, in most cases, $\omega_{AS}^{(0)} \neq \omega_{AS}^{(n)}$ and, therefore, $[\chi, H_0] \neq 0$ and the degree of chirality is always different from zero:

$$\chi \cong \cos\left(\frac{(\omega_{AS}^{(0)} - \omega_{AS}^{(n)})t}{2}\right)\cos\left(\frac{(\omega_{AS}^{(0)} + \omega_{AS}^{(n)})t}{2}\right)\tilde{\chi}. \tag{6}$$

The asymmetry excitation principle for the case of a racemic ensemble of chiral molecules requires that Eqs. (5) and (6) do not vanish at the averaging over all possible initial configurations of the molecules in the ensemble. With the use of this principle, an analysis of Eqs. (5) and (6) allows one to formulate respective conditions on the structure of the sequence of transitions used and on the parameters of the series of short pulses, namely,

(i) the number of transitions in the sequence must be odd; this prevents the use of biharmonic pumping in the laser distillation scenarios: the sequence of transitions along with the resonance two-photon transitions must include an odd number of one-photon transitions;

(ii) if n_α is the number of resonance fields with polarizations lying in the plane α and the rest of the $n_\perp$ fields have polarizations orthogonal to it (we suppose that all fields have linear polarizations), then $n_\perp$ must be an odd number; a similar condition must be fulfilled for the configuration of the dipole moments of the transitions in the sequence.

Constructing such a sequence of laser transitions that fulfill all the conditions listed above, as well as the selection rules for separate transitions, is, frankly speaking, a nontrivial problem and requires separate consideration. At this point, we just note that, for the specific case of a symmetric top molecule, the dipole moments of the ro-vibrational transitions of which coincide with the directions of the main tensor inertia axes, key limitations implied by the requirements discussed above and the selection rules coincide with each other.

3. INDUCING CHIRALITY IN H_2O_2 MOLECULES

In this section, we will apply the results of the previous section for inducing dynamical chirality in a racemic ensemble of H_2O_2 molecules with the help of a sequence of resonance picosecond laser pulses in the mid- and short-IR range (with frequencies of (4–11) × 10^{13} Hz) and maximum intensity of ~10^{12} W/cm^2. As the sequence of energy levels, we will use the low-lying deformational (ν_1 and ν_5) and valence (ν_2 and ν_6) modes, as well as different rotational sublevels of the ground vibrational state. The chiral properties of the molecule are described with the help of the Hund model [14], where θ is the torsional angle between the OOH planes (Fig. 2), which is called the reaction coordinate. Typical oscillation frequencies for the chirality for the low-lying vibrational states are of the order of (1–4) × 10^{11} Hz. In our calculations, we approximated the rotations of the molecule with the help of the symmetrical top model, which does not lead to errors due to the large difference in the masses of hydrogen and oxygen atoms.

The simplest scenario for the local excitation of chiral states in the molecule is the scheme with the use of three coherent laser pulses (the transition sequence is similar to that displayed in Fig. 3, II). For initial conditions with zero rotational temperature and with preliminary alignment of the z' axes, which determines the oxygen atoms' positions (Fig. 2), the amplitude of the oscillations of the degree of chirality can reach $\chi \sim 0.85$. Note that, for laser distillation scenarios in an ensemble of preliminary aligned molecules [3–9], the results are similar to those for our calculations. At zero translational temperature, under the assumption that all the molecules are frozen and after the averaging over all possible orientations of z', we get $\chi \sim 0.2$, whereas, with the rotations of the molecules around the O–O axes, we get $\chi \sim 0.1$. At the translational temperature $T \sim 300$ K, our calculations give $\chi \sim 10^{-3}$. Such a sharp decrease in the efficiency of the discussed scenario in comparison with zero temperature is due to the thermal excitation of a large number of rotational states of the molecules with which the laser pulses employed in the scenario do not interact.

The fact that we must use the coherent noncoplanar pulses leads to a difficulty in exciting the degree of chirality with the given spatial distribution of the chiral molecules in the ensemble, whose volume size is comparable to or larger than the wavelength. Nevertheless,

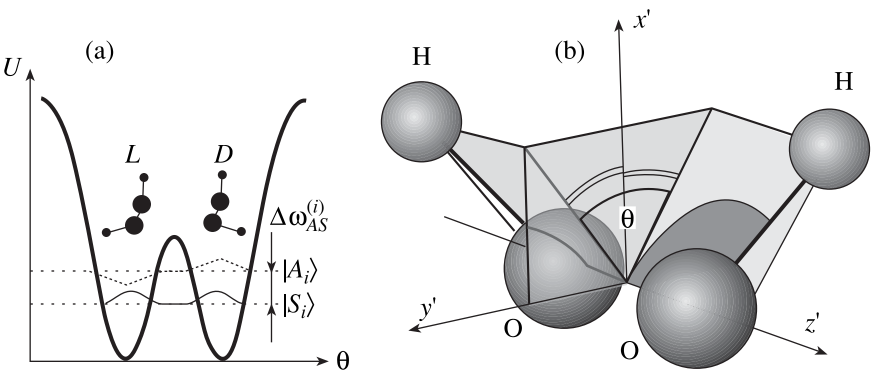

Fig. 2. Double-well ground-state potential $U(\theta)$ of the chiral H_2O_2 molecule (a) and Cartesian frame rigidly bound to the molecule (b), where θ is the dihedral angle formed by the planes crossing the oxygen atoms and one of the hydrogen atoms.

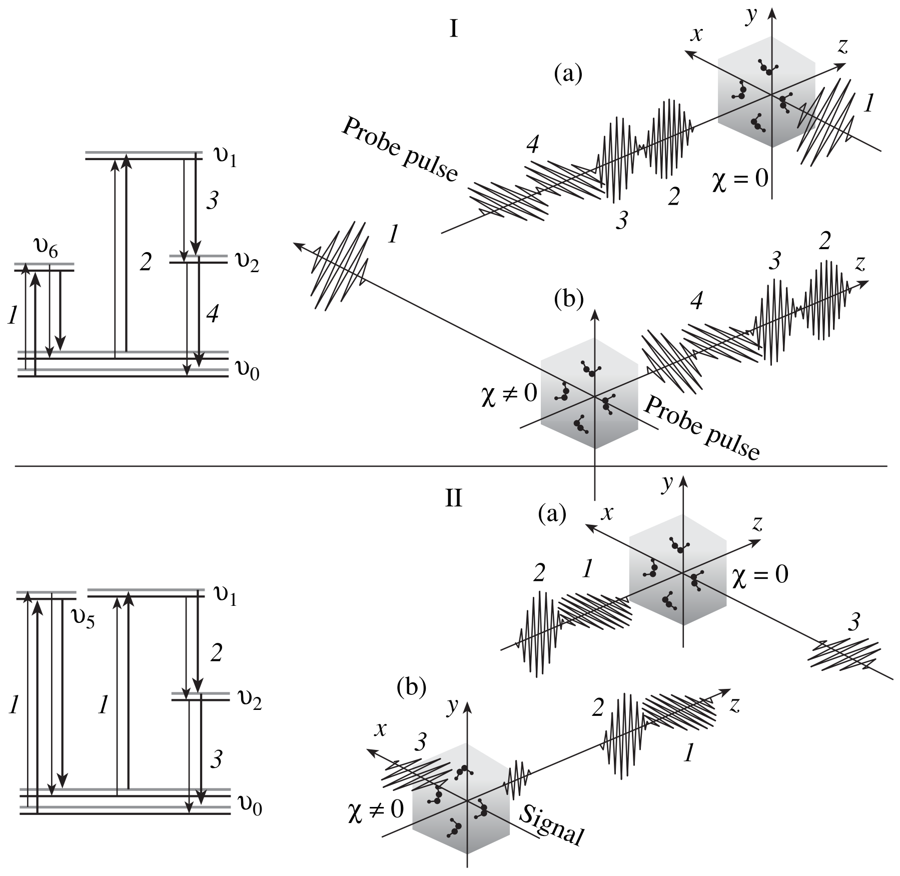

Fig. 3. Two possible laser distillation scenarios (I and II) in a randomly oriented ensemble of chiral molecules H_2O_2. Vibrational–rotational transitions employed in the specific scenario are shown on the left, where the numbers indicate respective pulses with corresponding frequencies. The spatial sequence of the laser pulses and their polarization configuration before (a) and after (b) interaction with the randomly oriented ensemble of chiral molecules are shown on the right (all laser pulses propagate along the respective Cartesian axes).

we can eliminate the phase dependency of the degree of chirality versus the phases of some laser pulses using different rotational sublevels of the vibrational level in the sequence of the resonant transitions employed in the scenario. The resulting scheme for both inducing and detecting the degree of chirality is shown in Fig. 3, I. Laser pulses *1–4* induce the degree of chirality; the result does not depend on the phase of the first laser pulse, and the phase of the oscillations of the degree of chirality weakly depends on z. Therefore, in connection with the induced degree of chirality, the optical activity in the ensemble of chiral molecules causes a unidirectional rotation of the polarization plane of the probe pulse. In the given field approximation, the requirements on the coherence of the pumped fields must be fulfilled on the scale of a few centimeters. However, in the saturated vapor of H_2O_2 molecules under normal conditions, our calculations give $\chi \sim 10^{-3}$, and the respective polarization rotation angle ~0.2''/cm; thus, it is difficult to measure such a rotation angle in an experiment.

Our investigations show that another laser distillation scenario that simplifies the detection of the induced chirality and that is shown in Fig. 3, II is more feasible for the possible applications. In this scenario, the chirality is first induced by three laser pulses *1–3* that result in the degree of chirality being spatially distributed on the grid with a volume ~1 mm^3. The detection can be made via registration of the linear quadruple response of the media on the probe pulse, for which we can use the tail of the third pulse. Selecting the direction of pulse propagation and adjusting the polarizations of laser pulses *1–3*, one can separate the direction of laser pulse propagation and polarization of the probe pulse and of the degree of chirality of the response pulse generated at the induced grid. The intensity of the response (signal) pulse in saturated vapor of H_2O_2 molecules under normal conditions is about 10^{-8} W/cm^2.

4. CONCLUSIONS

In conclusion, the analysis made in this paper allows us to propose a novel laser distillation scenario from a racemic solution of chiral molecules, as well as a detection scheme that does not require initial alignment of the ensemble of chiral molecules. This scenario employs excitation by short laser pulses of the sequence of resonance transitions in a chiral molecule specifically selected to follow the symmetry rules. This scenario works for small molecules with small energy splitting between chiral sublevels (the case of dynamical chirality). It is important to note that the suggested scenarios are all based on a coherent (quantum) entanglement of the molecule's rotational degrees of freedom with its chiral degrees of freedom. Therefore, the rotations of the chiral molecules and a careful analysis of them lie in the background of the problem. Specific calculations are made for the case of a racemic mixture of enantiomers of hydrogen peroxide molecules.

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